

# **Overview on C2 and C3 Selective Hydrogenation in Ethylene Plants**

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## **Introduction**

This paper will provide an overview on C2 and C3 selective hydrogenation operations in ethylene plants. The primary focus will be on selective hydrogenation of acetylene. The reason for this is that most C3 selective hydrogenation units installed since the mid-late 1970's are liquid phase units. For the most part, the details about the design and operation of liquid phase processes are proprietary, licensed technology.

This is an overview paper, providing background information for the succeeding papers in this session. The following papers will cover in more detail some experiences and know-how with acetylene and/or C3 selective hydrogenation within ethylene plants.

Acetylene and C3 hydrogenation units are purification steps for ethylene and propylene. Trace levels of acetylene, methyl acetylene (MA), and propadiene (PD) are formed in the steam cracking furnaces. The amount of acetylene and MAPD formed is a function of the furnace feed, along with furnace design and operating conditions. Acetylene will fractionate with ethylene; MAPD will fractionate with propylene. These components are only tolerable at < 1 ppm in polymer grade ethylene and propylene.

The overwhelmingly dominant method for removal of acetylene and MAPD is through selective hydrogenation. With few exceptions, acetylene hydrogenation is carried out, in vapor phase, adiabatic fixed bed reactors. The number of beds ranges from 1 to 4, with intercooling. Acetylene hydrogenation is also done with isothermal tubular reactors.

Liquid phase C3 hydrogenation became the "process-of-choice" around the mid-70's. The dominant process is an adiabatic, fixed-bed, liquid phase system. Some C3 liquid phase hydrogenation units have isothermal, tubular reactors. Many vapor phase C3 hydrogenation units are still in service.

During past Ethylene Producers Conferences (EPC), there have been several papers that deal with acetylene and C3 hydrogenation and the impact of contaminants on these operations. These are good reference documents. They are given in the "List Of References" for this paper.

This paper will cover the following items:

- **Acetylene Hydrogenation**
  - ✓ Options for locating hydrogenation units within ethylene plant sequences
  - ✓ Pros/Cons for Each Location
  - ✓ Operating Strategy
  - ✓ General Design Comments
  - ✓ Promoted Catalysts
  - ✓ Theory of Acetylene Hydrogenation
  - ✓ Green Oil
  - ✓ Comments on Contaminants
  - ✓ Regeneration Considerations

- **General Comments on C3 Hydrogenation**
- **Safety Considerations**

## Acetylene Hydrogenation

The basic requirements for acetylene hydrogenation units include the following:

- Safe operation; e.g., no exothermic runaway reactions; no “hot spots” during operation
- Maintain acetylene in ethylene product below specification. The typical maximum is 5 ppm; however, ethylene customers may expect the acetylene level to be maintained below 1 ppm; perhaps, below 0.5 ppm.
- Do not be the cause of interruptions to continuous operation of the ethylene plant; e.g., a target for continuous operation may be 5+ years.

Some secondary requirements or “very strong wishes” are:

- Operating with a net gain of ethylene; the higher, the better.
- “Low investment cost”---within the context of the overall cost considerations for ethylene plant investment, project execution, feedstocks, energy, etc.
- Good catalyst life and reasonable catalyst cost

## Location within the Ethylene Plant Process Sequence

An acetylene hydrogenation unit can be located at one of several locations within the ethylene plant sequence. There are two major designations for these locations: These are:

- Front-end
- Tail-end or Back-end

In the Front-End category, there are several possibilities. These are:

- DeC2 overhead in a DeC2-1<sup>st</sup> process sequence (Figure 1)
- DeC3 overhead in a DeC3-1<sup>st</sup> process sequence (Figure 2)
- Raw Gas: within the process gas compressor circuit, downstream of the caustic tower (Figure 3)

A subset for types of front-end hydrogenation units deals with the type of catalyst. The dominant catalyst is Pd-based, with the “modern” catalyst being bimetallic, palladium promoted with a second metal; e.g., with silver.

Another type of catalyst is sulfided NiCo. This catalyst was introduced 40+ years ago for front-end hydrogenation units. This catalyst operates with inlet temperatures that range from about 350 F (~175 C) to 450 F (~230 C). Sud Chemie still offers this catalyst, C-36, as a replacement catalyst for the “high temperature” units still in operation. This paper will not cover this type of selective hydrogenation unit. Major debits for this process are:

- The NiCo catalyst must be presulfided and maintained in a sulfided state via continuous injection of sulfur, in form of H<sub>2</sub>S, ethyl or n-butyl mercaptan, or DMDS,
- Typically, this hydrogenation unit operates with an ethylene loss.

The Tail-end or Back-end hydrogenation unit is associated with a demethanizer-first (DeC1-1<sup>st</sup>) ethylene recovery sequence. This unit is located upstream of the ethylene/ethane splitter, on the net DeC2 O/H. (Figure 4) At the tail-end location, hydrogen is injected into the reactor feed; whereas, with front-end hydrogenation units, all the hydrogen produced in the cracking furnaces is in the reactor feed.

### Comments about Acetylene Hydrogenation at Various Locations within Ethylene Plant Process Sequences

#### Front-End: Overhead of a Front-end DeC2

The feed to this hydrogenation unit contains the C<sub>2</sub> and lighter material. The feed is very rich in hydrogen and ethylene, particularly if the furnace feed is ethane. The only unsaturated reactants in the feed to this reactor are acetylene and ethylene. Some pros and cons about this location include the following:

#### Pros:

- Clean stream; i.e., no traces of BD to cause catalyst fouling
- Do not need a spare reactor
- High concentration of H<sub>2</sub> suppresses green oil formation
- Reactors are smaller, relative to the front-end DeC3 O/H system

### Cons:

- High concentration of H<sub>2</sub> may result in the operation being sensitive to initiation of ethylene hydrogenation; this may result in exothermic runaways
- Stability of operation is sensitive to CO fluctuations. This is because there is no MAPD in the feed to provide additional moderation.

### Front-End: Overhead of a Front-end DeC3

The feed to this acetylene hydrogenation unit contains the C<sub>3</sub> and lighter material. The feed is somewhat rich in hydrogen and ethylene. The primary difference between an acetylene hydrogenation unit in this location and one located in the front-end DeC<sub>2</sub> O/H is the presence of MAPD in the feed. Some pros and cons about this location include the following:

### Pros:

- Clean stream; however, there is the potential for the feed to contain traces of BD
- Moderately high concentration of H<sub>2</sub>; this suppresses green oil formation
- Presence of MAPD provides additional moderation that inhibits hydrogenation of ethylene, and hence, mitigates against exothermic runaways
- About 50 % of the MAPD is hydrogenated; essentially all of this is converted to propylene. This also means that any downstream C<sub>3</sub> hydrogenation facilities will be smaller.

### Cons:

- Acetylene plus MAPD impose a higher “load” on the reactor. This translates to higher overall heat rise, increasing the rate of catalyst fouling.
- Traces of BD may be in the converter feed; this will bring about additional catalyst fouling.
- May be difficult to operate without a spare reactor for continuous operation of 5+ years.
- Reactors are larger than for front-end DeC<sub>2</sub> O/H units

### Front-End: Raw Gas Location:

This reactor is placed within the process gas compressor circuit, downstream of the caustic tower, but upstream of the main driers. Hence, the feed to this acetylene hydrogenation unit is wet C5 and lighter, containing some C6's. Historically, this unit was designed for operation with sulfided NiCo catalysts. This type acetylene hydrogenation unit was installed in many ethane crackers designed/built in the mid 60's/early 70's.

For many years, Pd or Pd/promoter catalysts were not considered for this service. Some reasons for this include concerns that Pd-based catalysts were not "sufficiently rugged" for this severe service. In addition, it is known that water inhibits the activity of Pd catalysts, and it is known that water tends to increase the formation of green oil across Pd catalysts. However, our industry know-how is now such that ethylene plants are being designed and/or retrofitted with Pd/promoter catalysts in raw gas acetylene hydrogenation units. Hence, there have been some recent grass-roots designs with Pd/promoter catalysts in raw gas units, and there have been some conversions from sulfided NiCo to Pd/promoter.

### Pros:

- This operation will result in hydrogenation of C4 acetylenes and BD, hence minimizing the potential for fouling at bottom of downstream DeC2 and/or DeC3.
- Converts the majority of C3 and C4 acetylenes and diolefins into olefins, making the final C3 and C4 streams more attractive for fuel gas, and/or for recycle cracking.
- Contributes to other cost savings within the ethylene plant; for illustration, this allows for the elimination of a set of guard driers.

### Cons:

- Catalyst deactivation can be relatively rapid, especially for the first bed. This is primarily due to the presence of C4 and C5+ acetylene and diolefins. Hence, even with Pd/promoter catalysts, a spare reactor system is needed for continuous operation of 5+ years.
- May be difficult to maintain operation with an ethylene gain, especially if catalyst is sulfided NiCo
- Some acid species may be formed across the reactor. This may result in having to deal with downstream corrosion concerns.
- For sulfided NiCo catalyst, it is necessary to have a spare reactor system, along with facilities for insitu regeneration, reduction, and presulfiding. There are environmental concerns with handling sulfiding agents such as n-butyl mercaptan, ethyl mercaptan, DMDS, etc.

## Tail-End Location

The primary characteristics that differentiate this system from front-end systems are:

- The feed is C2's, the O/H of a backend DeC2.
- Hydrogen is controllably injected to each bed; typically at molar H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratios between 1.2 to 2.2.
- Green Oil, oligomers of acetylene, causes fairly rapid catalyst deactivation.
- There will be spare reactors with facilities for insitu catalyst regeneration and reduction. (Figure 5) Each reactor may be regenerated about 1-4 times a year.

Tail-end acetylene hydrogenation is one of the final steps in the recovery and purification of ethylene to produce polymer grade ethylene. This C<sub>2</sub>-stream may contain 0.5 to 2.5% acetylene. Some concerns/considerations with tail-end acetylene hydrogenation include:

- Acetylene will be upgraded to ethylene and downgraded to ethane and green oil (oligomers of acetylene, mostly C<sub>4</sub>'s with small amounts of C<sub>6</sub> to C<sub>20</sub>+ material)
- Tail-end units have downstream green oil (C<sub>6</sub>+) removal facilities
- Unreacted H<sub>2</sub> in the reactor effluent must be removed via a pasteurization section at the top of the ethylene/ethane splitter or via a downstream secondary demethanizer
- The character of the catalyst changes throughout the cycle. This change is primarily due to heavy green oil lay down on the catalytic sites. This change is temporary. The catalyst is "rejuvenated" via insitu steam/air regeneration followed by reduction with hydrogen.
- The character of the catalyst undergoes slow "permanent" changes through online operation and on being subjected to repeated regeneration. Catalyst life is 5+ years; perhaps, even 20+ years.
- Economic considerations drive operators toward optimizing tail-end hydrogenation units to maximize ethylene gain; however, this can make the operations vulnerable to acetylene breakthrough. An acetylene off-spec incident may result in a substantial production loss of ethylene; e.g., perhaps 1000+ Tons. This is because it takes several hours to eliminate acetylene from the ethylene/ethane splitter inventory.

A presentation to the 1999 EPC (Ref 34) is a good source for more information on the advantages and/or concerns with locations for the acetylene hydrogenation unit within ethylene plant sequences.

## Operating Strategy

The operating strategy for acetylene hydrogenation units is primarily based on staying within the operating window for selective stable performance. (Ref. 5, 6, 34, 35, 36) This means that acetylene will be hydrogenated, completely, and the hydrogenation of ethylene will be minimized. If the catalyst activity is too low, then acetylene leakage will occur. If the catalyst activity is too high, excessive ethylene hydrogenation will occur. The “location and size” of the operating window are affected by several parameters. These include:

- Inlet temperature
- Amount of hydrogen
  - ✓ For front-end units, this parameter is the hydrogen partial pressure.
  - ✓ For tail-end units, this parameter is the H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratio.
- Inlet acetylene, ---and inlet MAPD for front-end units located in DeC3 O/H
- Level of CO
- Space velocity----more of a problem for front-end units
- Trace catalyst poisons
- Catalyst type, e.g., promoted catalysts have larger operating window
- Condition of catalyst; e.g., new, old, history of runaways, amount of time online, etc.

### Front-end Acetylene Hydrogenation:

For front-end units, the only control parameter is the inlet temperature for each bed. Bed outlet acetylene level is used for feedback control of the inlet temperature. CO fluctuations in the feed present a control problem for these units. In addition, the operation becomes unstable at low space velocities; hence, the flow through the reactors must be maintained above a specified minimum.

### Tail-end Acetylene Hydrogenation:

There are two primary control parameters for the reactors at this location: Inlet temperature and the H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratio. Occasional changes may be made to the amount of CO being injected into the reactor feed. Movement “above” the operating window can be effected not only by increasing inlet temperature, but also by injecting too much hydrogen. High temperatures and/or high hydrogen injection rates will lead to non-selective performance, and consequently, acetylene leakage.

More information on modeling and control of acetylene hydrogenation units can be found in References 21 to 26.



## General Design Comments:

For front-end adiabatic units, the following provides illustrative design parameters:

- Space velocity for each bed: 8000-12000 V/V/Hr --Gas Volumetric Hourly Rate @ Std Cond./Cat. Vol.
- No. of beds in series, with intercooling:
  - ✓ Feed acetylene at/below 5000-6000 ppm: two beds
  - ✓ Feed acetylene between about 6000-7500 ppm: three beds
  - ✓ Feed acetylene between 7500-10,000 ppm: four beds

For tail-end adiabatic units, the following design parameters may apply:

- Space velocity for each bed: about 4000 V/V/Hr
- No. of Beds in series, with intercooling:
  - ✓ Feed acetylene at/below 5000 ppm: one bed
  - ✓ Feed acetylene between 0.5 and 1.7%: two beds
  - ✓ Feed acetylene between 1.7-2.5 %: three beds

More information on design/operating parameters for acetylene hydrogenation parameters can be obtained from the catalyst vendors and/or from References 34 through 36.

## Promoted or Bimetallic Acetylene Hydrogenation Catalysts

The “modern” or current generation of selective hydrogenation catalysts are often referred to as being promoted or bimetallic. (Ref. 8) Dow first reported the use of palladium/silver bimetallic catalysts for acetylene hydrogenation in 1957. (Ref. 1) However, Chevron Phillips and Sud Chemie gave the commercial impetus to bimetallic catalysts for acetylene hydrogenation by introducing a Pd/Ag catalyst into commercial service on the O/H from a front-end DeC2. (Refs. 2, 5, 6) This was done in the early ‘80’s. This work was aimed at achieving more stable, selective catalyst performance in service on a front-end DeC2 O/H stream.

- Chevron Phillips continued research on acetylene hydrogenation catalysts such that they now offer proprietary catalysts, designated “E Series” catalysts. (Ref. 5, 10, 34) These catalysts have been commercialized in several services; e.g., front-end DeC2 O/H, front-end DeC3 O/H, and raw gas.
- Sud Chemie offer a “family” of Pd/Ag catalysts for all front-end services and for tail-end acetylene hydrogenation. (Ref. 6, 35, 36) Sud Chemie’s front-end catalyst is designated G-83C. Their tail-end catalysts are: G-58C, G-58D, G-58E, G-58H, and G-58I.

- Katalena offer a front-end Pd/promoter catalyst designated 7741R. Their catalyst for tail-end service is 7741 A/F. Katalena do not provide information about the type of promoter used in formulating these catalysts. (Ref.34)
- Axens offer LT-279 for front-end and tail-end applications. Axens do not provide details on the promoter used in formulating this catalyst. (Ref. 3, 8)
- BASF offer HO-21 for tail-end acetylene hydrogenation. This catalyst is Pd, promoted with Ag. The support is silica oxide.

Details on the physical and chemical properties for these catalysts can be obtained from the vendors.

Here are some points on catalyst design taken from a paper by Chevron Phillips at the 1993 Ethylene Producers Conference: (Ref 5)

- The most active and selective catalysts occur when almost all of the Pd is within 300 microns of the surface.
- The addition of silver to the “Pd skin” catalyst offers a trade of a small loss in catalyst activity for a large increase in selectivity activity.
- There is an optimum silver loading: too much silver, while increasing selectivity reduces the activity to unacceptable low levels.
- Silver reduces the impact of variability in Pd distribution within the catalyst pellet.

### Comments on the Theory of Acetylene Hydrogenation

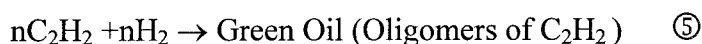
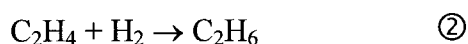
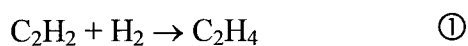
From the standpoint of an industrial operation, the theory of acetylene hydrogenation is, at best, imprecise. It is not possible to draw upon a well-formulated, well-understood body of science and apply such information to the industrial environment. There are a number of reasons for this:

- The primary one being the conversion of acetylene to green oil. This causes a change in the performance of the catalyst throughout a cycle. The change is much more rapid for a tail-end hydrogenation unit.

- Another reason is that most reported scientific information is for academic conditions; that is, with "new" catalysts, operating at low pressures, for short periods of time on synthetic feeds.
- The concentration of palladium deposited on the support is so small, e.g., 150-500 ppm; hence, it is very difficult to characterize these catalysts.
- The catalysts undergo changes time onstream and through successive regenerations.

### Reactions

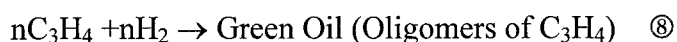
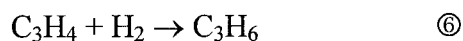
The reactions that can occur in tail-end acetylene hydrogenation units and acetylene hydrogenation units located in the O/H of a front-end DeC2 are listed below:



Reaction ① is desirable whereas reactions ② thru ⑤, are undesirable.

The amount of C<sub>2</sub>H<sub>2</sub> converted to C<sub>6</sub><sup>+</sup> in a front-end DeC2 O/H acetylene hydrogenation unit is much, much less than is the case for hydrogenation of C<sub>2</sub>H<sub>2</sub> across a tail-end unit.

In addition to reactions 1 through 5, the following reactions occur in an acetylene hydrogenation unit located on the O/H of a front-end DeC3.



Reaction ⑥ is desirable whereas reactions ⑦ thru ⑧ are undesirable.

Reactions ⑦ and ⑧ may not occur to a level of commercial significance in acetylene hydrogenation units located on the O/H of a front-end DeC3.

Reactions ⑥, ⑦, and ⑧ also occur in C3 hydrogenation reactors.

### Relative Adsorption

According to literature the rate of hydrogenation of ethylene in an ethylene-hydrogen mixture is 10-100 times faster than the rate of acetylene hydrogenation under identical conditions of temperature, pressure and catalyst. Thus the selectivity of acetylene hydrogenation can only be explained by the preferential adsorption of acetylene molecules on the surface of the palladium.

The rate of adsorption of hydrocarbons can be classified in the following decreasing order:

CO > Acetylenes >> Diolefins >> Olefins

Hence, kinetics is controlled by relative adsorption rates. The preferential adsorption of acetylene over ethylene means that provided there are sufficient acetylene molecules to cover all the active sites then ethylene hydrogenation to ethane is minimized. However, in an industrial operation, near the bottom of the final bed, where the acetylene concentration is reduced to about 1-5 ppm, a point is reached in the reactor bed where there is an insufficient number of acetylene molecules to maintain total active site coverage. Fortunately, carbon monoxide provides a means for blocking or inhibiting the adsorption of ethylene, since it has a higher rate of adsorption than that of ethylene. The CO molecules tend to occupy the active sites in the acetylene deficient regions.

For front-end acetylene hydrogenation units, CO will be in the reactor feed at a level of about 200-2000 ppm. For tail-end units, trace amounts of CO (0.1-5 ppm) can be injected into the reactor feed. Usually, this CO comes from bypassing a small stream of untreated hydrogen around the PSA unit or methanator.

## Oligomers (Green Oil) Formation

The following discussion pertains, primarily, to tail-end acetylene hydrogenation.

There is unanimous agreement in the literature that oligomers (green oil), C<sub>4</sub>'s and higher, are derived from acetylene and not ethylene. The subject of oligomers formation is one of high commercial importance but which is only discussed in patent literature and few published articles. The amount of green oil formation is primarily a function of the concentration of acetylene being converted. Hence, the rate of formation of green oil is higher on the lead bed where higher acetylene concentrations exist.

Discussion of fundamental causes of green oil formation engenders a lot of speculation. It doesn't form without the presence of hydrogen, and the amount formed decreases as the hydrogen partial pressure increases. Most researches agree that the precursor to all types of green oil produced in the selective hydrogenation of acetylene is 1,3-butadiene. This molecule is produced from hydrogenation of an acetylene dimer.

Catalyst deactivation by green oil becomes a major problem at very low hydrogen to acetylene ratios. Furthermore, the amount of green oil formation has been reported to be related to: surface acidity of the support, palladium crystallite size, mean pore size and pore size distribution, feed water content, and higher operating temperatures.

The net result of heavy green oil formation is a shortening of the catalyst cycle length and decrease in the catalyst selectivity.

About 10-20 % of the acetylene is converted to C<sub>4</sub> and heavier green oil. (Ref 3) The overwhelming majority is C<sub>4</sub>'s. The next major constituent is C<sub>6</sub>'s. A major improvement from the promoted catalysts is that the amount of heavy green oil polymers is substantially reduced. Hence, the rate of deactivation of the catalyst reduced.

Two industrial studies were found that dealt with green oil formation with Pd-only catalysts in industrial units. These studies were done using slipstream test units in ethylene plants in China and Russia (Ref. 11, 12). The Russian study reported that the green oils were composed of 23 wt % olefins, 2.5 wt % diolefins and 74.5 wt % aromatic compounds (Ref. 12).

The study carried out in China described the green oils as being long chained olefinic compounds with a general formula corresponding to C<sub>n</sub>H<sub>(1.8-1.9)n</sub> where n=14-17. These authors found that the quantity of aromatic compounds was negligible and that one quarter of the olefins was alpha olefins (Ref. 11).

Most of the published science on selective hydrogenation is based on studies with Pd-only catalysts. However, the latest generations of industrial acetylene converter catalysts are promoted with another metal; in many cases this is Ag. The following information comes from limited published information on the effect of Ag moderation on the Pd catalytic sites.

Axens(formerly Procatalyse) reported at the 1995 Spring AIChE Meeting that Ag moderation reduces C6+ formation but has no effect on formation of C4's. (Ref. 3) Axens compared the formation of green oil across a Pd-only catalyst with a Pd/Ag catalyst. Both catalysts were on an alumina support. The feed acetylene was 2.6 %. Here are some highlights from that paper.

- Oligomerization occurs via a first step of dimerization of acetylene on palladium sites and goes further through polymerization mechanisms to high molecular weight compounds. The C4s remain gaseous; the C6+ compounds are liquids and remain on the catalyst surface, reacting further to make even heavier hydrocarbons.
- The conversion of acetylene over a Pd-on-alumina catalyst showed that about 15% of the converted acetylene went to C4's and about 30 % of the converted acetylene went to C6+.
- The conversion of acetylene over the Pd/Ag catalyst showed that about 15% of the converted acetylene went to C4's and the amount of acetylene converted to C6+ was substantially reduced.
- The amount and type of C4's formed was independent of the addition of silver to the catalyst.
- The amount of acetylene converted to ethylene was increased on addition of the silver.

An excerpt from a Sud Chemie brochure on the effect of Ag on green oil formation is as follows: (Ref 35)

"This decrease in the production of green oil is accomplished by the use of Ag in conjunction with the palladium hydrogenation metal. In essence, Ag acts like an atomic spacer to increase the distance between the active palladium sites. This lessens the chance for two molecules of acetylene to combine to form the 1,3-butadiene precursor, leading directly to less potential polymer formation."

Sud Chemie has reported laboratory data to illustrate the effect of Ag on reducing the amount of heavy green oil formed during hydrogenation of acetylene. This illustration is provided in Figure 6. The amount of polymer formation with the promoted catalyst is only about 40% of the amount produced with the Pd-only catalyst.

### Catalyst Poisons and Inhibitors of Pd Catalysts:

Typical ethylene plant contaminants that can cause problems for acetylene and C3 selective hydrogenation catalysts are CO, H<sub>2</sub>O, H<sub>2</sub>S, and mercaptans. Methanol also causes problems. Other Pd catalyst poisons frequently encountered include COS, arsine,